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# Enrichment of Chromium at Grain Boundaries in Chromia Doped $UO_2$

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ABSTRACT

Assessment of grain boundaries in chromia ($Cr_2O_3$) doped fuels has been carried out using high resolution transmission electron microscopy to assess the structure compared to undoped fuel produced via the same process. Chemical analysis of the grain boundary was carried out using Energy Dispersive X-ray Spectroscopy (EDS). It was shown that a relatively disordered phase is formed along the grain boundaries in the doped fuel and that they were chemically enriched in chromium. This has implications for the prediction and understanding of fuel manufacture and in-reactor behaviour as many processes are highly dependant on grain boundary mechanisms.



Chromia doped fuels are being considered as an evolutionary accident tolerant fuel (ATF) candidate [1] due to their reported changes in mechanical properties [2], altered fission gas release [3,4] and improved washout behaviour [5]. These properties are expected to vary as a result of the deviations that occur in the post-sintered microstructure. Originally, these dopants were used to improve the sinterability of $UO_2$, particularly from conversion routes such as the AUC (ammonium uranyl carbonate) conversion process [3,5,6], however efforts to understand further operational benefits are being assessed by the international nuclear fuel community.

The mechanism by which the dopants produce the larger grains is not fully understood. A range of investigations, both experimental and theoretical, have tended towards two, not necessarily competing, mechanisms: (1) an increase in bulk diffusivity that therefore increases the grain size during sintering [4] and (2) an increase in grain boundary diffusivity, again increasing the grain size. As noted, multiple mechanisms may be occurring simultaneously or dependant on dopant concentration and sintering atmosphere. For example, in the work of Bourgeois et al. [7], two distinct peaks in grain size are present at different dopant concentrations in the sample sintered in 1 vol.% $H_2O + H_2$ at ~600 $\mu$g $(Cr_2O_3)/g(UO_2)$ and ~2500 $\mu$g $(Cr_2O_3)/g(UO_2)$ indicating the likelihood of multiple grain growth mechanisms.

Mechanism (1) requires some bulk solubility in the $UO_2$ matrix, and then a large enough impact to cause quite a marked microstructural change, whilst Mechanism (2) requires low solubility species existing at grain boundaries and surfaces of $UO_2$ rather than in solid solution in order to maximise the concentration and impact on the grain boundary, but not too much to cause grain boundary pinning or a seizure in sintering. The presence of grain boundary phases may also alter the defect chemistry of the bulk system. Recent theoretical work has shown that the formation of disordered or amorphous grain boundary phases have much higher thermodynamic drives to deviate their stoichiometry compared to the crystalline bulk $UO_2$ [8], and therefore may alter the bulk material's stoichiometry. This will alter the sintering behaviour of the fuel and also will change subtle properties such as bulk material lattice parameters [9].

The solubility of Cr in $UO_2$ has been assessed on a number of occasions. Experimentally, the solubility has been estimated as 0.07 wt.% (700 wppm) by Bourgeois et al. [7] and a thorough evaluation was provided by Riglet-Martial et al. [10] to ranging from 500 wppm to 1000 wppm (for $Cr_2O_3$). It is regularly noted

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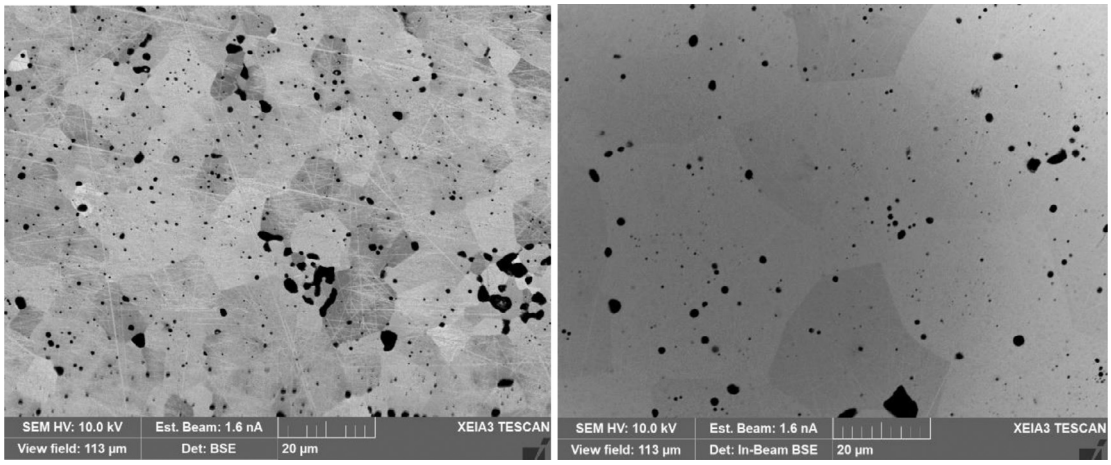


**Fig. 1.** Back-scattered electron micrograph images of undoped (left) and Cr-doped UO2 analysed in this study. Grain size enlargement is clearly shown in the doped fuel.

in literature that once the solubility limit of $Cr_2O_3$ in $UO_2$ is exceeded, grain growth is reduced. Some emphasis was placed onto the oxidation state of Cr entering the $UO_2$ matrix. It was noted that at high temperatures and low oxygen partial pressures, the Cr may reduce to a 2+ charge state, thus altering the solution route [4] with conflicting experimental observations that may be made clearer with the use of single crystal data in the future. A solubility model was put forward by Riglet-Martia [10] highlighting the potential reduction of Cr to a 2+ charge-state at high sintering temperatures and intermediate to high oxygen partial pressures (avoiding the formation of Cr metal) and the formation of $CrO_{(l)}$. The solubility model did not consider alterations to chemistry that could be present at grain boundaries and the impact of grain boundaries as defect sinks.

Killeen [3] performed some of the seminal work on Cr-doped $UO_2$ and highlighted, amongst other things, the segregation of Cr to grain boundaries during operation and therefore highlighting the instability of solute Cr at the dopant levels tested (0.5 wt.% in this study) as well as possible co-migration mechanisms with fission gases from the bulk to the grain boundaries.

The solubility of Al in $UO_2$ is reported to be negligible according to Kashibe and Une [11] and Lang [12]. This very low solution energy agrees with theoretical results performed using empirical potentials [13]. Solubility values are low and the mechanism for grain growth observed, for example by Kashibe [11] from 15 $\mu$m in the undoped sample to 30 $\mu$m in the 760 wppm $Al_2O_3$ sample, is presently not clear (especially as the redox behaviour of $Al_2O_3$ is markedly less varied compared to $Cr_2O_3$). Similarly, grain growth is observed in MgO doped $UO_2$ [12] and $TiO_2$ doped $UO_2$ [14], both known to have very low solubilities in $UO_2$ that are unlikely to impact intrinsic processes to produce changes in grain sizes observed experimentally. Specifically on $TiO_2$ as a dopant, Silva et al. [14] performed a study that assessed the dopant's impact when added through a sol-gel process where the resulting grain size was >300% than that of the un-doped fuel. Secondary Ti-rich phases were observed at grain boundaries and a reduction in grain size was also observed that was attributed to some solute Ti within the bulk, possibly as a result of the low-temperature gelation method. Indeed, it should be noted that the synthesis route chosen will significantly alter the distribution and behaviour of the additions to $UO_2$, and mix-milling of powders (as is generally the production route for commercial fuels) [15] can only be compared to sol-gel and wet synthesis methods [9,16] with care.

Other work has considered the formation of a ternary or mixed U-Cr oxide and its implications. $CrUO_4$ was first reported by Brisi [17] and then Hoekstra [18]. Subsequently, experimental work has highlighted the assumed charge states of both Cr and U in this compound to be 3+ and 5+, respectively [19]. Solubility of Al into this structure was both theoretically predicted and experimentally verified, potentially providing some answers as to the changing behaviour when co-doping $Al_2O_3$ with $Cr_2O_3$ into the $UO_2$ system that may be pointing towards other mechanisms that dictate grain growth in $Cr_2O_3/Al_2O_3$ doped fuels. The formation of $CrUO_4$ in the early stages of sintering could act as a key intermediate in the sintering behaviour of Cr-doped fuel, forming readily with $UO_{2+x}$ [19], and the formation of the Al-containing $(Cr,Al)UO_4$ may enhance the effect of this intermediate compound at some stage of the sintering process. Further work assessing the potential beneficial impact of this intermediate is required.

Grain boundary complexion and structure is known to impact many synthesis and in-operation mechanisms of ceramics. First and foremost, the changing structures of grain boundaries have been strongly linked to changing in grain boundary mobility and diffusion mechanisms [20,21]. Grain boundaries can be considered in groups depending on the order at the grain boundary, and if there is a distinct film or phase between the two crystallites. Complexion IV noted to be "a true wetting film because it has a thickness that depends only on the amount of available liquid phase (i.e. the thickness would diverge in a glass melt)" [22].

This work uses pellets produced via a commercial route to investigate the grain boundary structure and composition produced as a result of doping. The doped pellet's structure is compared to an un-doped fuel. The aim is to assess whether Cr is observed to segregate to grain boundaries, to assess the resulting grain boundary structures and to add to the body of work investigating the role of $Cr_2O_3$ and other relatively insoluble additives to $UO_2$.

Production of $Cr_2O_3$ and $Al_2O_3$ doped $UO_2$ pellets was carried out at Westinghouse Electric Sweden's Västerås facility. AUC converted $UO_2$ powder (with O/U stoichiometry of 2.14) was mixed with 500 wppm of $Cr_2O_3$ and 150 wppm $Al_2O_3$ for approximately one hour to obtain full homogeneity. It is important to note that according to the existing literature, the $Cr_2O_3$ concentration is expected to be below the solubility limit.

The doped powder was pressed to green pellets with a force of approximately 49 kN. The green pellets were sintered in a $H_2/CO_2$ atmosphere at a maximum temperature of 1770 °C. Previous work by Arborelius et al. has reported expected properties and parameters of the pellets produced by this method (equivalent to pellet D3 in that work) [5].

A standard undoped $UO_2$ pellet was produced using similar sintering conditions (1730–1750 °C in a $H_2/N_2$ atmosphere) to compare to the doped pellet. This was produced at the Springfields

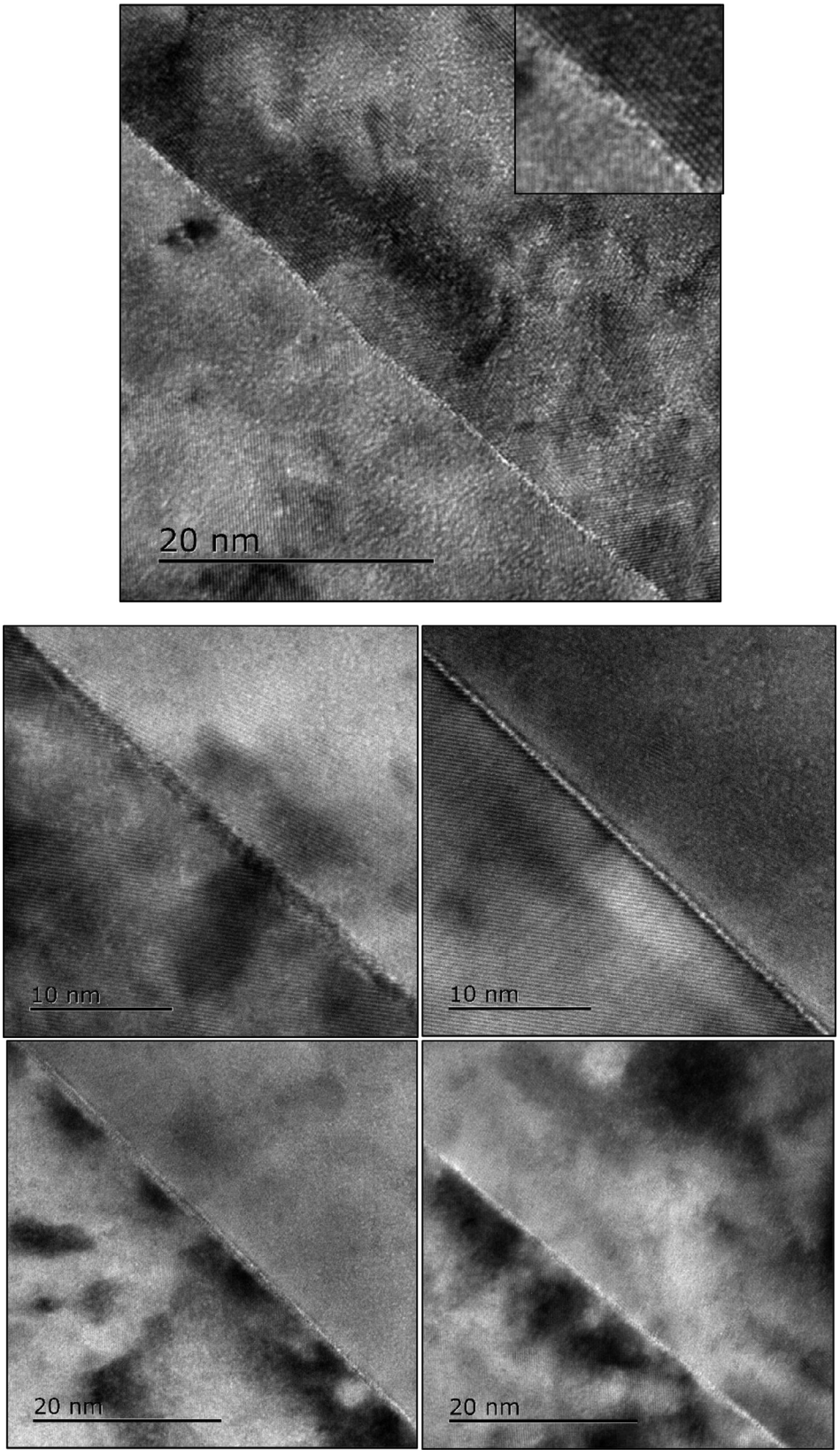


**Fig. 2.** Top: High resolution transmission electron microscopy (HRTEM) image from the Cr-doped $UO_2$ pellet including a grain boundary. Inset is a higher magnification of a portion of the grain boundary. Below: other examples of HRTEM images of grain boundaries in the Cr-doped pellet.

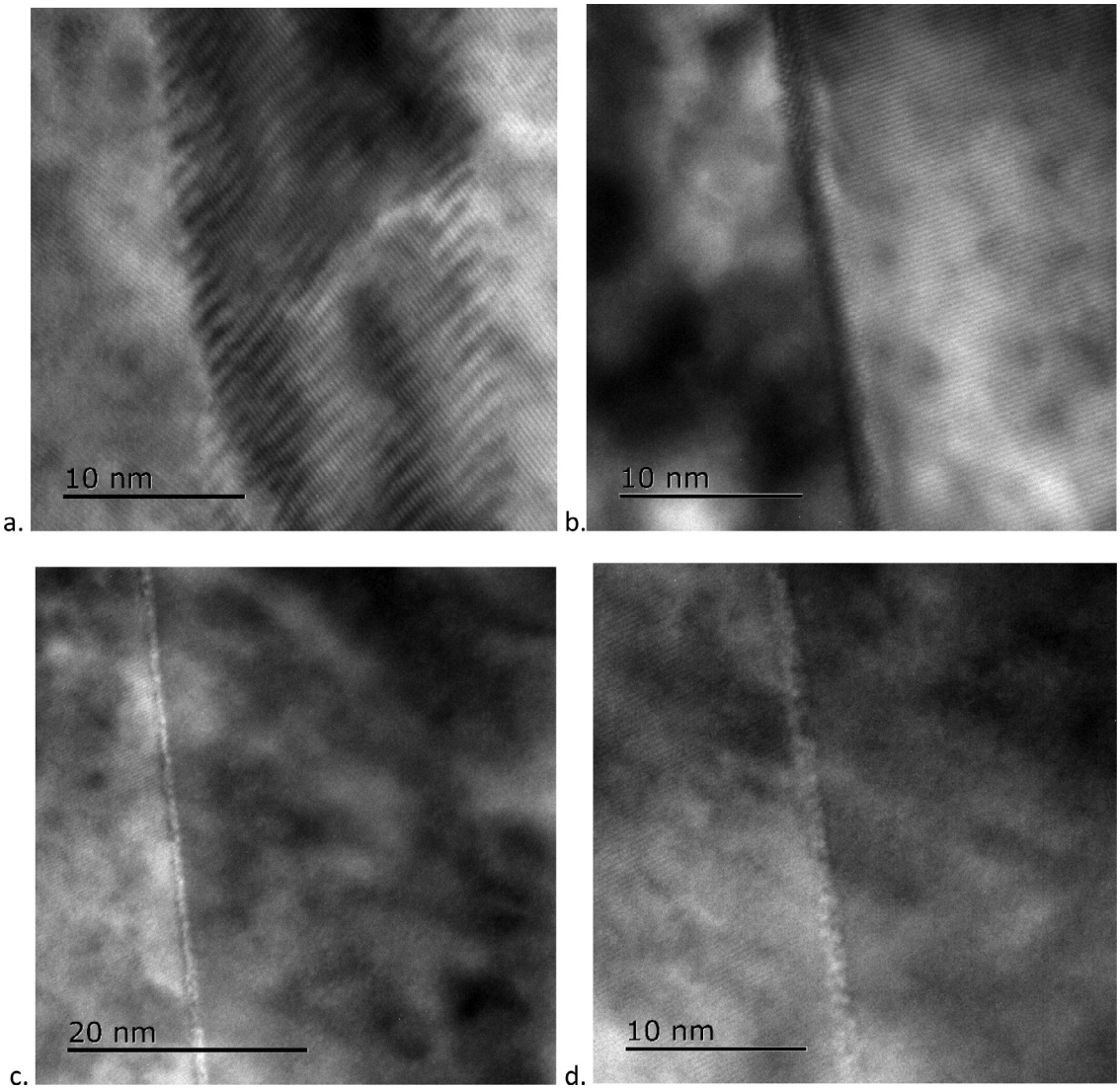


**Fig. 3.** Examples of high resolution microscopy of four grain boundaries observed in the undoped $UO_2$ sample.Top (a&b): grain boundaries with very little thickness/disorder observed and Bottom (c&d): grain boundaries with a thickness similar to the doped sample.

Fuels Ltd manufacturing facility using $UO_2$ converted through the integrated dry route. Final stoichiometries of both pellets were determined to be in the range 2.00–2.02 through X-Ray Diffraction lattice parameter measurements.

Sample examination was carried out using both Tescan XEIA3 plasma focused ion-beam and FEI Helios 600i focused ion-beam (FIB) instruments, the latter was used for transmission electron microscope (TEM) sample preparation. Fig. 1 shows the back-scattered electron micrograph image of the un-doped and doped fuels highlighting the significant increase in grain size upon doping with $Cr_2O_3$. These images were used to identify grain boundaries that were subsequently targeted for further analysis. Lamella samples were extracted from the bulk cross-section samples and then thinned to approximately 150 nm thickness using varying ion beam energies and final stages of preparation conducted at 5 kV and a final cleaning polish at 2 kV was used.

Samples were then examined in a JEOL 2100 TEM with a $LaB_6$ electron source operated at 200 kV and equipped with an Oxford Instruments Ultimax X-ray detector and AZtec software. Overview images were taken in bright-field TEM mode and high resolution TEM (HR-TEM) was used to examine the grain boundary structures. Scanning transmission (STEM) mode was used to obtain compositional maps and line profiles across grain boundaries using energy-dispersive X-ray analysis (EDX).

High resolution transmission electron microscopy (HR-TEM) was undertaken on both the Cr-doped and undoped $UO_2$ samples after sample preparation. The sections prepared were specifically targeted to assess the grain boundary nature of the ceramics. Fig. 2 provides a micrograph of a grain boundary in the Cr-doped $UO_2$. The atomic ordering in the grains either side of the boundary is distinct, highlighting that the grain boundaries themselves are somewhat disordered although there appears to be evidence of some diffusive ordering, similar to the theoretical predictions proposed by Rushton et al. [23] related to glass-crystal interfaces.

In regions of the grain boundary reported in Fig. 2, the thickness of the grain boundary can be seen to be 2–3 atomic planes thick, indicating a complexion III or IV system as defined by Dillon et al. [22]. The nature of the grain boundary appears ordered in some regions and disordered in other regions, especially those that are thicker. This observation is also in line with categorising the grain boundaries in the Cr-doped samples as complexion II or IV boundaries. These bi-layers or tri-layers have been shown to impact a number of properties including atomic transport that may impact the sintering and operation of such materials.

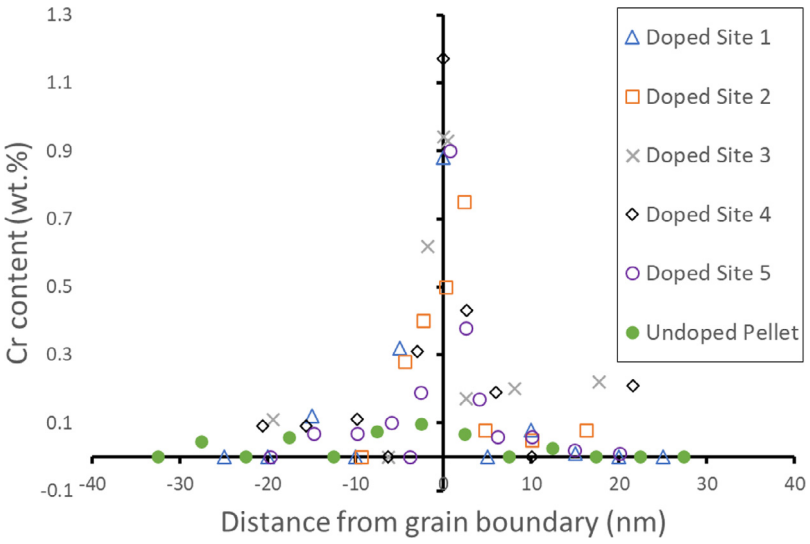


**Fig. 4.** Chromium concentration as a function of distance from the grain boundary assessed by EDX spectroscopy.

When assessing the grain boundary structure of the undoped system, the thickness of the grain boundary film varied considerably from nearly zero thickness (Fig. 3a and 3b) to similar thicknesses observed in the doped samples (Fig. 3c and 3d). This variation in grain boundary type is commensurate with previous experimental work assessing grain boundaries using electron backscattered diffraction (EBSD) techniques [24] that determined that coincident site lattice (CSL) boundary fraction was of the order of 15% of the observed grain boundaries.

Chemical assessment of the grain boundaries was undertaken using EDX analysis. In the doped fuel system, a number of line scans were carried out across grain boundaries and are reported in Fig. 4. Due to the interaction region of the EDX analysis, the resolution around the grain boundary is not sharp, however there is a clear enrichment of Cr observed at the grain boundary. This indicates that the Cr is not in complete solid solution within the bulk of the system, which provides data to aid the mechanistic understanding of not only grain growth in these large-grained doped fuels, but will also be important to consider when assessing the material's behaviour in reactor. As expected, the undoped pellet did not show any enrichment of Cr at the grain boundary.

The implications of the observations are important when considering the development and use of doped fuels that enhance grain boundaries. These results highlight that the solubility of Cr into the bulk, even at the low dopant levels of 500 wppm $Cr_2O_3$, is not complete when considering the commercial route for pellet production and that Cr will be affecting the behaviour of grain boundaries during the sintering process and during operation. Sintering atmospheres, temperatures and profiles are known to impact the solubility and behaviour of Cr in the $UO_2$, and in addition to affecting the bulk behaviour, the sintering atmosphere will also be altering the structure and chemistry of the grain boundary.

The possible stabilization of higher complexity grain boundaries will likely impact the character of grain boundary bubbles that form containing fission gases, and the mobility of fission products along the grain boundary. Further work should be carried out to assess the role of Cr within the grain boundary structure on the mobility of fission gases and volatile species along them, altering their transport to the rod free volume. Our findings build upon the experimental findings from Killeen [3], who reported significant grain boundary segregation of Cr in Cr-doped fuel after irradiation. Further work should assess the source of the diffuse grain boundary observations of Killeen and whether the source could be a combination of bulk Cr moving to boundaries or whether the high concentration of Cr at the grain boundaries acted as the source of the diffuse Cr regions.

Experimental work has identified that creep is higher in Cr-doped fuels and alumino-silicate doped pellets [2]. The alteration in grain boundary structure and chemistry observed in this investigation provides a basis for this observation and highlights that Coble creep mechanisms are altered in doped fuels.

Future work should also consider the implications of the findings in this investigation on phenomena such as high burnup structure formation, the impact of the grain boundaries as sinks for defects and non-stoichiometry as well as the implications of grain boundary attack by corrosive species and steam relevant to washout events where a cladding structure has failed.

In conclusion, the present investigation has undertaken a high-resolution transmission electron microscopy assessment on doped and undoped $UO_2$ pellets post sintering. The grain boundary structure of the doped fuel was observed to have been altered in the doped fuel system and chemical analysis highlighted the enrichment of Cr at the grain boundaries in the doped fuel system. The observation has implications to the mechanistic understanding of the production and operation of doped fuels.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Megan Owen reports financial support was provided by Westinghouse Electric Simon Middleburgh reports financial support was provided by Westinghouse Electric.

## CRediT authorship contribution statement

**Simon C. Middleburgh:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing, Supervision. **Simon Dumbill:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Data curation, Investigation. **Adam Qaisar:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Data curation, Investigation. **Ian Vatter:** Methodology, Formal analysis, Data curation, Investigation. **Megan Owen:** Formal analysis, Writing – original draft. **Sarah Vallely:** Methodology, Formal analy-

sis, Writing – original draft, Investigation. **Dave Goddard:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Resources, Writing – review & editing. **David Eaves:** Conceptualization, Writing – review & editing, Resources. **Mattias Puide:** Conceptualization, Writing – review & editing. **Magnus Limbäck:** Funding acquisition, Resources. **William E. Lee:** Writing – original draft, Writing – review & editing, Funding acquisition.

## Data availability

Data will be made available on request.

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## References

[1] Y. Che, G. Pastore, J. Hales, K. Shirvan, Modeling of $Cr_2O_3$-doped $UO_2$ as a near-term accident tolerant fuel for LWRs using the BISON code, Nuclear Eng. Design 337 (2018) 271–278.
[2] J. Wright, C. Anghel, S. Middleburgh and M. Limback, "Fuel hardware considerations for BWR PCI mitigation," in *Top Fuel 2016: LWR Fuels With Enhanced Safety and Performance*, Boise, ID (USA), 2016.
[3] J. Killeen, Fission gas release and swelling in $UO_2$ doped with $Cr_2O_3$, J. Nucl. Mater. 88 (1980) 177–184.
[4] M. Cooper, G. Pastore, Y. Che, C. Matthews, A. Forslund, C. Stanek, K. Shirvan, T. Tverberg, K. Gamble, B. Mays, D. Andersson, Fission gas diffusion and release for $Cr_2O_3$-doped $UO_2$: from the atomic to the engineering scale, J. Nucl. Mater. 545 (2021) 152590.
[5] J. Arborelius, K. Backman, L. Hallstadius, M. Limback, J. Nilsson, B. Rebensdorf, G. Zhou, K. Kitano, R. Lofstrom, G. Ronnberg, Advanced Doped $UO_2$ Pellets in LWR Applications, J. Nucl. Sci. Technol. 43 (2006) 967–976.
[6] I. Greenquist, M. Tonks, M. Cooper, D. Andersson, Y. Zhang, Grand potential sintering simulations of doped $UO_2$ accident-tolerant fuel concepts, J. Nucl. Mater. 532 (2020) 152052.
[7] L. Bourgeois, P. Dehaudt, C. Lemaignan, A. Hammou, Factors governing microstructure development of $Cr_2O_3$-doped $UO_2$ during sintering, J. Nucl. Mater. 297 (2001) 313–326.
[8] S.C. Middleburgh, W.E. Lee, M.J.D. Rushton, Structure and properties of amorphous uranium dioxide, Acta Mater 202 (2021) 366–375.
[9] P. Kegler, M. Klinkenberg, A. Bukaemskiy, G. Murphy, G. Deissmann, F. Brandt, D. Bosbach, Chromium Doped $UO_2$-Based Ceramics: synthesis and Characterization of Model Materials for Modern Nuclear Fuels, Materials (Basel) 14 (2021) 6160.
[10] C. Riglet-Martial, P. Martin, D. Testemale, C. Sabathier-Devals, G. Carlot, P. Matheron, X. Iltis, U. Pasquet, C. Valot, C. Delafoy, R. Largenton, Thermodynamics of chromium in $UO_2$ fuel: a solubility model, J. Nucl. Mater. 447 (2014) 63–72.
[11] S. Kashibe, K. Une, Effect of additives ($Cr_2O_3$, $Al_2O_3$, $SiO_2$, MgO) on diffusional release of Xe from $UO_2$ fuels, J. Nucl. Mater. 254 (1998) 234–242.
[12] S. Lang, High-temperature Reactions of Uranium Dioxide With Various Metal Oxides, National Bureau of Standards Circular 568, Washington DC (USA), 1956.
[13] S.C. Middleburgh, D. Parfitt, R.W. Grimes, B. Dorado, M. Bertolus, P.R Blair, L. Hallstadius, K. Backman, Solution of trivalent cations into uranium dioxide, J. Nucl. Mater. 420 (2012) 258–261.
[14] C. Silva, R. Hunt, A. Nelson, Microstructural and crystallographic effects of sol-gel synthesized Ti-doped $UO_2$ sintered under reducing conditions, J. Nucl. Mater. 552 (2021) 153003.
[15] C. Silva, R. Hunt, K. Holliday, An evaluation of tri-valent oxide ($Cr_2O_3$) as a grain enlarging dopant for $UO_2$ nuclear fuels fabricated under reducing environment, J. Nucl. Mater. 553 (2021) 153053.
[16] H. Smith, L. Townsend, R. Mohun, T. Cordara, M. Stennett, F. Mosselmans, K. Kvaahnina, C. Corkhill, $Cr^{2+}$ solid solution in $UO_2$ evidenced by advanced spectroscopy, Communs. Chem. 5 (2022) 163.
[17] C. Brisi, The uranate of the $MU_3O_{10}$ type, Ann Chim 53 (1963) 325.
[18] H. Hoekstra, Some uranium-transition element double oxides, Adv. Chem. 71 (1967) 211–227.
[19] M. Cooper, D. Gregg, Y. Zhang, G. Thorogood, G. Lumpkin, R. Grimes, S. Middleburgh, Formation of (Cr, Al)$UO_4$ from doped $UO_2$ and its influence on partition of soluble fission products, J. Nucl. Mater. 443 (2013) 236–241.
[20] S. Dillon, M. Harmer, J. Luo, Grain boundary complexions in ceramics and metals: an overview, JOM 61 (2009) 38–44.
[21] S. Dillon, M. Harmer, Relating grain-boundary complexion to grain-boundary kinetics i: calcia-doped alumina, J. Am. Ceram. Soc. 91 (2008) 2304–2313.
[22] S. Dillon, M. Tang, W. Carter, M. Harmer, Complexion: a new concept for kinetic engineering in materials science, Acta Mater. 55 (18) (2007) 6208–6218.
[23] M. Rushton, R. Grimes, S. Owens, Partial ordering of glass networks adjacent to simulated glass–crystal interfaces, J. Non Cryst. Solids 357 (2011) 3278–3287.
[24] P. Nerikar, K. Rudman, T. Desai, D. Byler, C. Unal, K. McClellan, S. Phillpot, S. Sinnot, P. Peralta, B. Uberuaga, Grain boundaries in uranium dioxide: scanning electron microscopy experiments and atomistic simulations, J. Am. Ceram. Soc. 94 (6) (2011) 1893–1900.